International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:11, No:12, 2017

Nanofluid-Based Emulsion Liquid Membrane for Selective Extraction and Separation of Dysprosium

Maliheh Raji, Hossein Abolghasemi, Jaber Safdari, Ali Kargari

Abstract**—**Dysprosium is a rare earth element which is essential for many growing high-technology applications. Dysprosium along with neodymium plays a significant role in different applications such as metal halide lamps, permanent magnets, and nuclear reactor control rods preparation. The purification and separation of rare earth elements are challenging because of their similar chemical and physical properties. Among the various methods, membrane processes provide many advantages over the conventional separation processes such as ion exchange and solvent extraction. In this work, selective extraction and separation of dysprosium from aqueous solutions containing an equimolar mixture of dysprosium and neodymium by emulsion liquid membrane (ELM) was investigated. The organic membrane phase of the ELM was a nanofluid consisting of multiwalled carbon nanotubes (MWCNT), Span80 as surfactant, Cyanex 272 as carrier, kerosene as base fluid, and nitric acid solution as internal aqueous phase. Factors affecting separation of dysprosium such as carrier concentration, MWCNT concentration, feed phase pH and stripping phase concentration were analyzed using Taguchi method. Optimal experimental condition was obtained using analysis of variance (ANOVA) after 10 min extraction. Based on the results, using MWCNT nanofluid in ELM process leads to increase the extraction due to higher stability of membrane and mass transfer enhancement and separation factor of 6 for dysprosium over neodymium can be achieved under the optimum conditions. Additionally, demulsification process was successfully performed and the membrane phase reused effectively in the optimum condition.

Keywords**—**Emulsion liquid membrane, MWCNT nanofluid, separation, Taguchi Method.

I. Introduction

THE rare earth elements (REEs) are a group of metals comprised of 14 elements of the lanthanide series, yttrium, and scandium. REEs and their compounds are crucial for a broad and rapidly growing range of applications because of their unique physical and chemical properties. Their special chemical, electrochemical, catalytic, optical and magnetic properties stem from their unsaturated 4f electronic structure [1], [2]. These elements are widely used in petroleum, metallurgy, textiles, medical, nuclear, and optical industries. They are also incorporated into components of wind turbines, LEDs, capacitors, disc drives, mobile phones, and hybrid cars. In addition, lanthanides are critical components for radar, navigation, and night vision goggles, and defense technologies [1], [3]. Permanent magnets are the most essential parts in electrical, electronics, and medical devices in many high-tech industries. Neodymium(Nd) permanent magnets are tetragonal alloys of neodymium, iron, and boron which have been applied in various sectors requiring a high energy product and high coercive force [1], [4]. The addition of dysprosium(Dy) to the permanent magnets can enhance the corrosion resistance of them and improve magnetic properties of the product [5]. Dy is also used in the production of special ceramic compositions with BaTiO formulations [6]. Different applications of lanthanides in the electronic and other industries have resulted in increased demand for high purity of them [3]. Nevertheless, the primary resources of REEs are limited. Thus, separation and purification of these metals from secondary resources is necessary. On an industrial scale, solvent extraction and ion exchange are usually employed to separate and purify REEs encountering various difficulties. In order to overcome these difficulties, developing viable and efficient alternatives to removal and recovery methods are needed [7]. Since the invention of ELM, which is an advanced technique of solvent extraction, it has been renowned as a novel method for separating and concentrating metal ions [8].

ELM has received considerable attention by a host of researchers which is attributed to its outstanding characteristics such as large surface area available within the emulsion globules and internal droplets, lower volume ratio of organic phase to aqueous feed solution in comparison with conventional liquid-liquid extraction, and energy saving [9], [10].

Nanoparticles can be efficiently used to stabilize emulsions. For example, carbon nanotubes (CNT) have received considerable attention because of their numerous applications in liquid-liquid interfaces such as enhanced oil recovery, drug delivery capsules, diesel engine, and pickering emulsions [11]–[14]. It is also reported that mass transfer rate increases in liquid-liquid extraction by using different nanoparticles (CNT, ZnO and TiO_2) [15].

The objective of this paper is using nanofluid-based ELM for Selective Extraction and Separation of Dysprosium. For this purpose, MWCNT was used for preparing the nanofluids. The experiments were designed by using Taguchi method in order to investigate the influences carrier concentration, MWCNT concentration, feed phase pH and stripping phase concentration on the separation factor of Dy over Nd. Then, the optimum level for each factor was determined.

M. Raji is with Center for Separation Processes Modeling and Nano-Computations, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran (e-mail: Maliheh_raji@ut.ac.ir).
H. Abolghasemi is with Center for Separation Processes Modeling and Nano-Computations, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran (email: hoab@ut.ac.ir).
J. Safdari is with the Nuclear Fuel Cycle Research School, Nuclear Science and Technology Research Institute, Tehran, Iran (e-mail: jsafdari@aeoi.org.ir).
A. kargari is with Membrane Processes Research Laboratory (MPRL), Department of Petrochemical Engineering, Amirkabir University of Technology, Mahshahr Campus, Mahshahr, Iran (e-mail: kargari@aut.ac.ir).

II. Materials & Methods

A. Chemicals

Cyanex 272 (bis (2, 4, 4-trimethylpentyl) phosphinic acid) as mobile carrier, and sorbitan monooleate which is commercially known as Span 80 as surfactant were provided by Sigma Aldrich (Germany). Dysprosium(III) nitrate hexahydrate (Dy $(NO_3)_3 \cdot 6H_2O$, 99.9%purity) and Neodymium (III) nitrate hexahydrate (Nd $(NO_3)_3 \cdot 6H_2O$, 99.9 % purity) were product of Middle East Ferro Alloy Company (Iran). Nitric acid (HNO_3 (65%)) as internal stripping phase was obtained from Merck. The MWCNTs with mean diameter of less than 8 nm, length of 30 μm, and purity of more than 98% were purchased from the Research Institute of the Petroleum Industry (RIPI, Tehran, Iran). The other chemical reactants were analytically graded and were used directly as received from the company.

B. Experimental Procedure

In the first step, 2% (v/v) of Span 80 and appropriate amount of Cyanex 272 were mixed in kerosene as diluent. Then, nanofluid-based liquid membrane was prepared by dispersing required amounts of MWCNT to the organic solution using a homogenizer (Ultra-Turrax IKA T18, Germany) at 15000 rpm for 5 min followed by sonication in an ultrasonic bath (DSA 100-SK2, DESEN, 120 W,40 kHz, China) for 30 min. After that, nitric acid was added dropwise to the nanofluid-based liquid membrane under stirring at 6000 rpm during 10 min, to make a milky-white W/ emulsion. The volume ratio of internal stripping to membrane phase was 0.5 in all of the experiments.

Stock solution of 50 mg/L Dy and 50 mg/L Nd was prepared by dissolving appropriate amount of (Dy $(NO_3)_3 \cdot 6H_2O$ and Nd $(NO_3)_3 \cdot 6H_2O$ in distilled water and its pH value was adjusted. In fact, the feed phase solution contained equal amount of both metals and the prepared emulsion was dispersed in it by an overhead stirrer at 240 rpm during the extraction time of 10 min. the treat ratio (ratio of feed to membrane phase) was 10.

Samples of 5 mL were taken, and secondary emulsions were filtered by using a filter paper (Whatman, No.1, USA) and laboratory to separate the primary emulsion from feed solution. Dy and Nd concentration in the internal stripping phase was determined. Then, the selectivity of Dy over Nd was calculated by measuring the separation factor (β), which is defined as:

$$\beta = \frac{(C_i/C_j)_{Stripp}}{(C_i/C_j)_{Feed,0}} \tag{1}$$

where C_i and C_j are the concentrations of Dy(III) and Nd(III) in the stripping and initial feed solutions.

All experimental runs were performed at constant temperature (25 ±0.5 °C). In this study, demulsification was carried out by heating the emulsions to 80 °C and centrifugation at 5000 rpm in 3 min.

C. Experimental Design

Taguchi method is a standardized form of experimental design technique in which effects of several factors are studied simultaneously. By applying this method, the number of experiments required to optimize the selected key variables reduces. In addition, the influence of individual factors, the optimum level for each factor, and the most important factor is determined. In this paper, the L_9 orthogonal array of Taguchi is used to investigate the effect of four factors in three levels. The L and the subscript 9 demonstrate the Latin square and the number of experiments, respectively [16], [17]. The levels of the factors studied for the separation process through ELM and experimental layout design are shown in Tables I and II, respectively.

TABLE I
EXPERIMENTAL RANGE OF OPERATING PARAMETERS AND THEIR CORRESPONDING LEVELS

Parameters	Levels		
	L_1	L_2	L_3
A- Carrier Concentration (M)	0.5	1	1.5
B- Feed phase pH	0.5	2	4
C- Internal Concentration(M)	0.5	1	2
D- MWCNT Concentration(%wt)	0	0.05	0.1

TABLE II
EXPERIMENTAL LAYOUT DESIGN USING THE L_9 ARRAY

Run	A	B	C	D
1	0.5	0.5	0.5	0
2	0.5	2	1	0.05
3	0.5	4	2	0.1
4	1	0.5	1	0.1
5	1	2	2	0
6	1	4	0.5	0.05
7	1.5	0.5	2	0.05
8	1.5	2	0.5	0.1
9	1.5	4	1	0

III. Results & Discussion

The performance of ELM can be affected by some factors known as controllable or uncontrollable (noise sources). In order to observe the effects of uncontrollable factors on the process, each experimental run was repeated twice at the same conditions. Furthermore, the mean response for each run and an appropriately chosen signal-to-noise ratio (SN) were used to analyze the results. The analysis has three steps; determination of the effect of chosen variables and interactions, a statistical ANOVA, and determination of the optimum condition.

A. Effect of the Variables and Interactions

The main effects of the four chosen process variables of nanofluid-based ELM for selective extraction of Dy were examined using Taguchi method with the arrangement of Table II. According to (2), the larger-the-better performance characteristic was employed to obtaining the maximum selectivity of Dy over Nd:

International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:11, No:12, 2017

$$SN_L = -10\log\left(\frac{1}{n}\sum\frac{1}{y_i^2}\right) \qquad (2)$$

where n is the number of experiments and y_i is the response at each experiment. In these experiments, the optimum condition obtained when the response (selectivity) was as large as possible [18]. The experimental responses are presented in Table III.

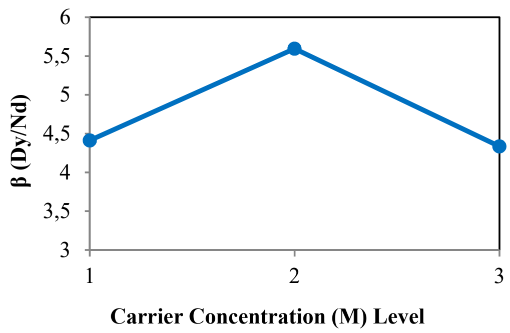
TABLE III
EXPERIMENTAL RESULTS FOR THE SELECTIVITY

Run	Selectivity ($\beta_{Dy/Nd}$)			
	Trial#1	Trial#2	Mean Value	S/N Ratio
1	3.163	3.09	3.126	9.899
2	6.902	6.711	6.806	16.655
3	3.268	3.334	3.301	10.371
4	6.768	6.589	6.678	16.491
5	5.587	5.003	5.295	14.437
6	4.718	4.9	4.809	13.636
7	3.354	3.567	3.46	10.77
8	4.854	5	4.927	13.848
9	4.915	4.322	4.618	13.236

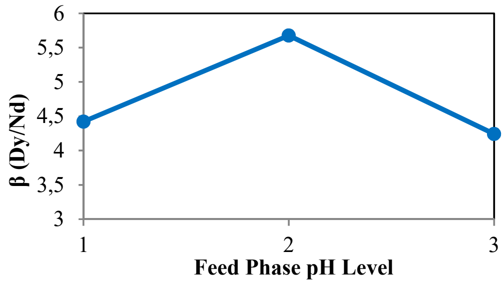
The results of responses in each level are summarized in Table IV. The effects of each factor on selectivity and SN_L ratio are given in Figs. 1 and 2.

TABLE IV
RESULTS OF RESPONSE FOR TAGUCHI ANALYSIS OF THE SELECTIVITY DATA

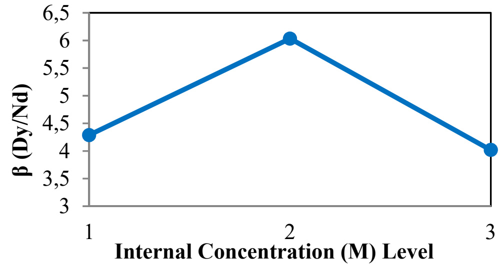
Levels	Response			
	A	B	C	D
L_1	4.411	4.421	4.287	4.346
L_2	5.594	5.676	6.034	5.025
L_3	4.335	4.242	4.018	4.968
$L_1 - L_2$	-1.184	-1.255	-1.747	-0.68
$L_1 - L_3$	0.075	0.179	0.269	-0.622
$L_2 - L_3$	1.259	1.434	2.016	0.057



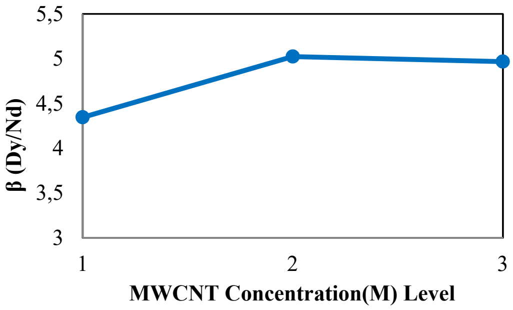
(a)



(b)



(c)



(d)

Fig. 1 (a) Effect of carrier concentration on selectivity (b) Effect of feed phase pH on selectivity(c) Effect of Internal concentration on selectivity (d) Effect of MWCNT Concentration on selectivity

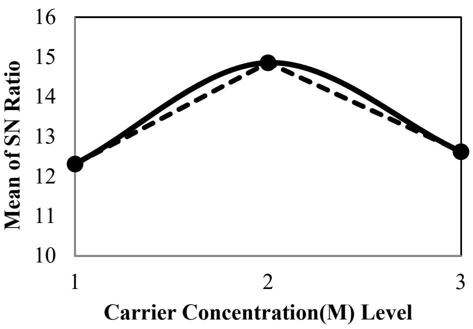
Fig. 1 (a) indicates the main effects of carrier concentration on selectivity of Dy over Nd. This factor directly affects the amount of both metal extractions. In fact, increasing carrier concentration improves the selectivity, because it forms a complex with the species to be transported and carries them into the membrane. On the other hand, when its concentration increased from 1 to 1.5 M, results in lower extraction, enrichment, and the separation factor value. This is due to the increase in viscosity of the membrane, which limits the amount of extraction with increase in mass transfer resistance. Furthermore, increasing the carrier concentration over a certain limit decreases the stability of the emulsion [16].

Main effects of feed phase pH on selectivity are shown in Fig. 1 (b). With respect to this figure, pH increase of the feed phase from 0.5 to 2 results in an increase in selectivity initially. But, as the pH is further increased, the separation factor value decreases due to the increasing co-extraction of Nd. In addition, when pH of the feed phase is increased the osmotic pressure difference increases leading to swelling of the membrane.

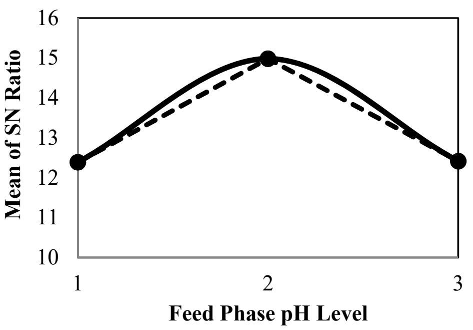
In this study, HNO_3 has been selected as the appropriate reagent as the internal stripping phase. According to Fig. 1 (c), by increasing the internal phase concentration, the ability of internal phase for stripping the complex at the external surface of internal droplets is increased. Thus, the separation factor of 6.034 was obtained at nitric acid concentration of 1 M. It shows that further increase in concentration of stripping solution reduced the value of separation factor due to decreasing the extent of extraction, stripping, and enrichment of both metals ions and membrane swelling enhancement [5].

The main effects of MWCNT concentration on the selectivity of the ELM are depicted in Fig. 1 (d). It can be seen that the separation factor increases by increasing MWCNT concentration up to 0.05 wt.% and shows a decrease thereafter. This can be explained by the fact that growing MWCNT percentage in membrane leads to more stabilized emulsion leading to increase the extraction. Nevertheless, when MWCNT concentration reaches a certain value, further increase leads to the growth of membrane phase-internal phase interfacial viscosity and mass transfer resistance which can also affect the separation factor. These findings are in agreements with our previous work for samarium extraction through nanofluid-based ELM [14].

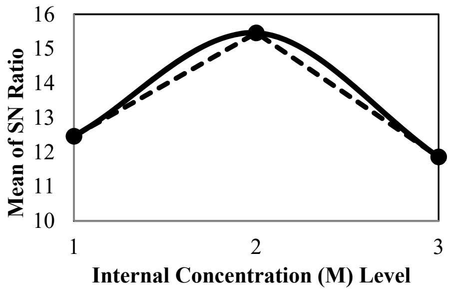
According to Fig. 2, the effect of each factor on SN_L ratio shows similar trends of its effect on selectivity and the factor levels maximizing the SN_L ratio are optimal.



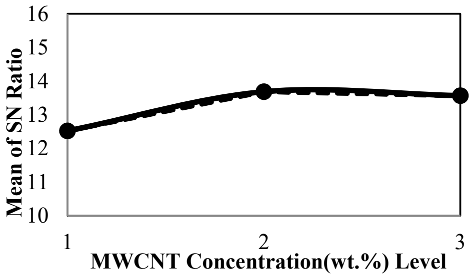
(a)



(b)



(c)



(d)

Fig. 2 (a) Effect of carrier concentration on SN_L ratio (b) Effect of feed phase pH on SN_L ratio (c) Effect of internal concentration on SN_L ratio (d) Effect of MWCNT concentration on SN_L ratio

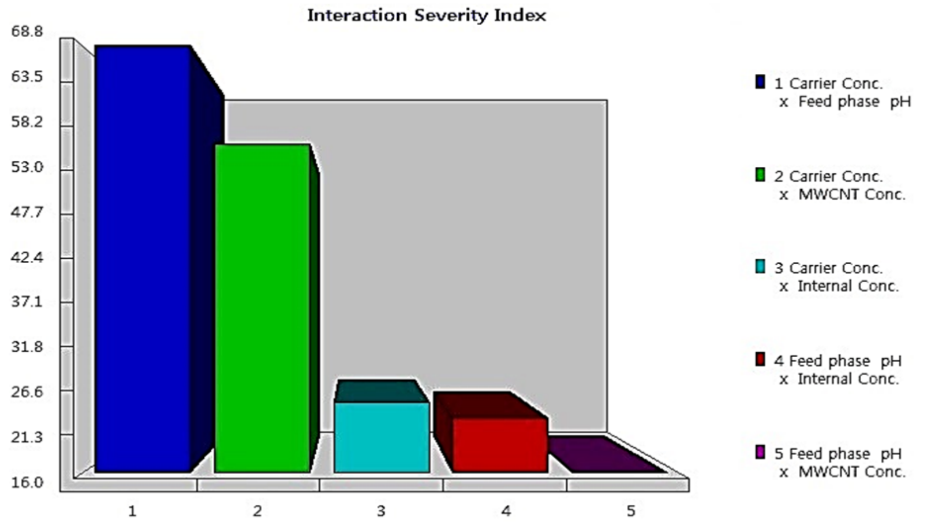
The results of analysis of interaction between the factors are shown in Fig. 3. It is clear from the interaction bar that the strongest interaction is between the carrier and pH of the feed phase (68.8%). It may be attributed to the mechanism of lanthanides pertraction with acidic carriers. Indeed, pH gradient between the feed phase and the internal phase is the driving force for the diffusion of metal ion-carrier complex molecules through the membrane [5].

It should be noted that the second important is between the carrier and MWCNT concentration which may be attributed to their influence on the membrane stability.

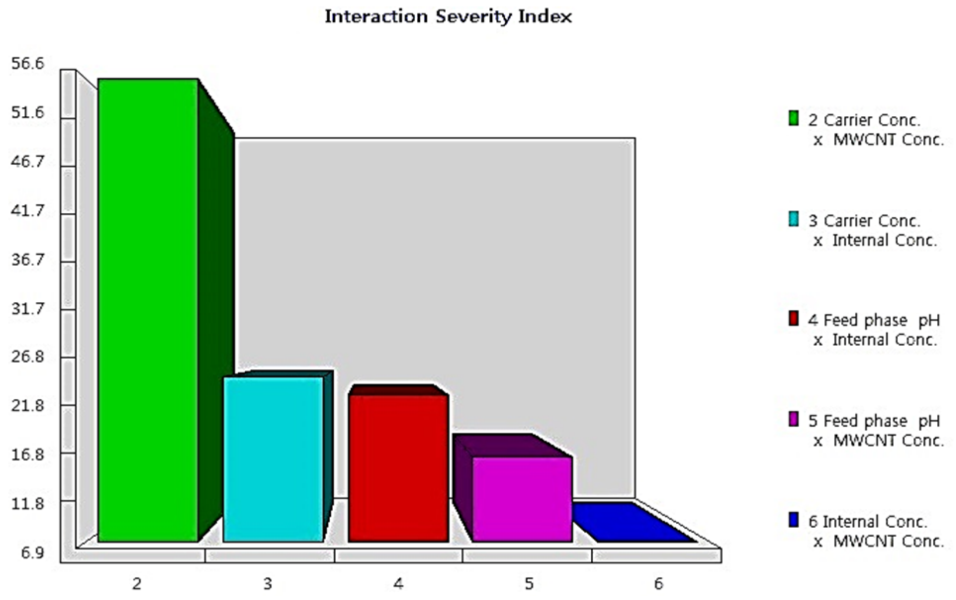
B. Analysis of Variance (ANOVA)

A statistical ANOVA was performed to observe the effective parameters and their significant level. The results of ANOVA are listed in Table V. In this table, DOF is the degree of freedom for each factor. SS denotes the sum square of the errors, and variance shows the deviation of the results from the average value. Percent represents the percentage of contribution or probability percent. The more the percent, the more is the influence of the related factor on the selectivity.

With respect to Table V, the internal phase concentration significantly affects the performance of ELM for selective extraction and separation of Dy. Based on the results, internal phase concentration, pH of the feed phase, carrier concentration, and MWCNT concentration have the most effects on the performance characteristic, respectively. As stated above, internal phase concentration is the most significant extraction process factor due to its highest percentage contribution, that is, 47.894%. The contribution of error is 2.761 %, which is within a reasonable range of error.



(a)



(b)

Fig. 3 Results of the percentage of interaction among the process factors (a) interaction severity index for percentage of interaction less than 70% and comparison of them(b) interaction severity index for percentage of interaction less than 60% and comparison of them

TABLE V
RESULTS OF STATISTICAL ANOVA

Factors	DOF	SS	Variance	F-Ratio	Pure Sum	Percent
A	2	5.979	2.989	61.809	5.882	19.732
B	2	7.319	3.659	75.668	7.222	24.229
C	2	14.374	7.187	148.595	14.277	47.894
D	2	1.701	0.85	17.591	1.604	5.384
Error	9	0.435	0.048	-	-	2.761
Total	17	29.81				100%

C. Optimization of the Variables

We conducted the statistical optimization of operating parameters and the optimal experimental condition corresponding to a maximum of the separation factor value is presented in Table VI. Under the optimal condition, the maximum predicted separation factor was 7.987.

In order to developing an economically feasible ELM process, the possibility of reuse of the organic membrane solution is an important aspect. To examine the recycle performance, we collected the demulsified membrane phase of the optimum experiment of this design and reused it to test the separation factor.

After determination of the optimum conditions using the statistical analysis, the confirming experiments were carried out at these conditions in order to test the predicted results. Under the optimum operating conditions in this work, the value of the separation factor by fresh membrane was 7.22. Under the same experimental condition, the value of separation factor by the reused membrane was 6.35. Hence, the organic membrane solutions recycled from the spent emulsions were reusable in the ELM process without any significant decline in its performance for selective separation of Dy.

TABLE VI
OPTIMIZED DATA USING TAGUCHI METHOD

Factors	Optimum Level	Level Description
A- Carrier Concentration (M)	2	1
B- Feed pH	2	2
C-Internal Concentration (M)	2	1
D-MWCNT Concentration (% wt)	2	0.05

IV. CONCLUSION

The present study revealed that nanofluid-based ELM could be effectively applied for selective extraction and separation of Dy from aqueous solution. Various factors affecting selective extraction such as carrier concentration, MWCNT concentration, feed phase pH and stripping phase concentration were investigated in details. Optimal experimental conditions for selective extraction and separation of Dy from aqueous solutions containing an equimolar mixture of Dy and Nd were obtained using ANOVA after 10 min extraction as Cyanex 272 concentration of 1 M; feed phase pH of 2, stripping phase concentration of 1 M; and MWCNT concentration of 0.05 wt.%. Results show that the use of nanofluids as liquid membrane phase leads to higher extraction efficiency and separation factor due to their stability and mass transfer enhancement. Under the optimum conditions, the experimental value of separation factor (7.22) was in satisfactory agreement with that predicted (7.987).

The nanofluid-based ELM was reused after demulsification for economical consideration and no noticeable decline in separation factor and extraction performance was observed.

The findings of the study open a future possibility of extending the nanofluid-based ELM for extraction and separation of the other metal ions used in various industries.

REFERENCES

[1] F. Xie, T. A. Zhang, D. Dreisinger, F. Doyle, A critical review on solvent extraction of rare earths from aqueous solutions, Miner. Eng. 56 (2014) 10–28. doi:10.1016/j.mineng.2013.10.021.

[2] R. Torkaman, M. A. Moosavian, J. Safdari, M. Torab-Mostaedi, Synergistic extraction of gadolinium from nitrate media by mixtures of bis (2,4,4-trimethylpentyl) dithiophosphinic acid and di-(2-ethylhexyl) phosphoric acid, Ann. Nucl. Energy. 62 (2013) 284–290. doi:10.1016/j.anucene.2013.06.028.

[3] B. Swain, E. O. Otu, Competitive extraction of lanthanides by solvent extraction using Cyanex 272: Analysis, classification and mechanism, Sep. Purif. Technol. 83 (2011) 82–90. doi:10.1016/j.seppur.2011.09.015.

[4] H. Yoon, C. Kim, K. W. Chung, S. Kim, J. R. Kumar, Recovery Process Development for the Rare Earths from Permanent Magnet Scraps Leach Liquors, J. Braz. Chem. Soc. 26 (2015) 1143–1151.

[5] M. Raji, H. Abolghasemi, J. Safdari, A. Kargari, Pertraction of Dysprosium from Nitrate Medium by Emulsion Liquid Membrane Containing Mixed Surfactant System, Chem. Eng. Process. Process Intensif. (2017). doi:10.1016/j.cep.2017.06.010.

[6] P. Zaheri, H. Abolghasemi, T. Mohammadi, M.G. Maraghe, Dysprosium pertraction through facilitated supported liquid membrane using D2EHPA as carrier, Chem. Pap. 69 (2015) 279–290. doi:10.1515/chempap-2015-0007.

[7] M. Anitha, D. N. Ambare, D. K. Singh, H. Singh, P. K. Mohapatra, Extraction of neodymium from nitric acid feed solutions using an emulsion liquid membrane containing TOPO and DNPPA as the carrier extractants, Chem. Eng. Res. Des. 98 (2015) 89–95. doi:10.1016/j.cherd.2015.04.011.

[8] G. Kakoi, Takahiko, Nishiyori, Takayuki, Oshima, Tatsuya, Kubota, Fukiko, F. Masahiro, Shinkai, Seiji, Nakashio, Extraction of rare-earth metals by liquid surfactant membranes containing a novel cyclic carrier.php.pdf, J. Memb. Sci. 136 (1997) 261–271.

[9] P. Davoodi-Nasab, A. Rahbar-Kelishami, M. Raji-Asadabadi, Fast and efficient chromium(VI) pertraction with Aliquat 336 in emulsion liquid membrane using sunflower oil as a high potential solvent, Desalin. Water Treat. 80 (2017) 234–246. doi:10.5004/dwt.2017.20990.

[10] H. Jiao, W. Peng, J. Zhao, C. Xu, Extraction performance of bisphenol A from aqueous solutions by emulsion liquid membrane using response surface methodology, Desalination. 313 (2013) 36–43. doi:10.1016/j.desal.2012.12.002.

[11] I. Akartuna, A. R. Studart, E. Tervoort, U. T. Gonzenbach, L. J. Gauckler, Stabilization of oil-in-water emulsions by colloidal particles modified with short amphiphiles, Langmuir. 24 (2008) 7161–7168. doi:10.1021/la800478g.

[12] J. S. Basha, R. B. Anand, An experimental investigation in a diesel engine using carbon nanotubes blended water-diesel emulsion fuel, Proc. Inst. Mech. Eng. Part a-Journal Power Energy. 225 (2011) 279–288. doi:10.1177/2041296710394247.

[13] N. M. Briggs, J. S. Weston, B. Li, D. Venkataramani, C. P. Aichele, J. H. Harwell, S. P. Crossley, Multiwalled Carbon Nanotubes at the Interface of Pickering Emulsions, Langmuir. 31 (2015) 13077–13084. doi:10.1021/acs.langmuir.5b03189.

[14] M. Raji, H. Abolghasemi, J. Safdari, A. Kargari, Optimization of Samarium Extraction via Nanofluid- Based Emulsion Liquid Membrane Using Cyanex 272 as Mobile Carrier, Int. J. Chem. Mol. Nucl. Mater. Metall. Eng. 11 (2017) 145–149.

[15] A. Mirzazadeh Ghanadi, A. Heydari Nasab, D. Bastani, A.A. Seife Kordi, The Effect of Nanoparticles on the Mass Transfer in Liquid–Liquid Extraction, Chem. Eng. Commun. 202 (2014) 600–605. doi:10.1080/00986445.2013.858037.

[16] S. M. Mousavi, S. Kiani, M. R. Farmad, A. Hemati, B. Abbasi, Extraction of Arsenic(V) from Water Using Emulsion Liquid Membrane, J. Dispers. Sci. Technol. 33 (2012) 123–129. doi:10.1080/01932691.2010.548230.

[17] A. Elmenshawey, A. Abdelrazak1, A. M. Mowafey1, Yehia Osman, Optimization of Bioreactor Cultivation Parameters by Taguchi Orthogonal Array Design for Enhanced Prodigiosin Production, Preprints (2017) 2017010002 .doi:10.20944/preprints201707.0002.v1

[18] P. Kazemi, M. Peydayesh, A. Bandegi, T. Mohammadi, O. Bakhtiari, Stability and extraction study of phenolic wastewater treatment by supported liquid membrane using tributyl phosphate and sesame oil as liquid membrane, Chem. Eng. Res. Des. 92 (2014) 375–383. doi:10.1016/j.cherd.2013.07.023.